PATENT SPECIFICATION

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(54) TAGGING EXPLOSIVES WITH ORGANIC MICROPARTICLES

(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 3M Center, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns the tagging of explosives for retrospective identification, even after detonation.

U.S. Patent No. 3,772,200 and our United Kingdom Patent Specification No. 1,441,419 disclose a method of tagging individual units of production of a substance from an inventory of batches of microparticles of a refractory carrier material of characteristic shape and size. Each batch of microparticles is uniformly coded by selected combinations and concentrations of tagging elements. By incorporating a uniquely coded batch of microparticles in each unit of production, the recovery and analysis of a single microparticle with an electron microprobe analyser is sufficient to identify the unit of production. When incorporated into sticks of dynamite, the microparticles were recoverable from debris of the explosion. When incorporated into ammunition, the microparticles were recoverable from the projectiles, spent cartridges, gun barrels and from matter through which the projectiles passed. However, the explosives industry has declined to adopt that invention on the grounds that the refractory microparticles tend to increase the sensitivity of explosives to accidental detonation, especially when added to the Talley mixer in the manufacture of dynamite where solid dopants are blended directly with liquid nitroglycerine.

Hence, there continues to be a need for a safe method of tagging explosives that would enable law enforcement officers to trace the source of explosives after detonation.

The present invention provides an explosive composition comprising (A) explosive material and (B) microparticles of a tack-free organic carrier which does not have a softening point below 60° C., which microparticles have a distinctive shape, contain one or more tagging elements in uniform amounts of at least 0.1 percent of the total weight, and which are capable of surviving detonation of the explosive material and so permit retrospective identification of the explosive although it has been detonated. Surprisingly, the organic microparticles provide positive identification of explosives after detonation without increasing the sensitivity of the explosives to accidental detonation. In fact, a wide variety of organic carriers provide microparticles which apparently reduce the sensitivity of dynamite and yet are recoverable from the debris of an explosion.

To facilitate recovery, the shape of the microparticle should be sufficiently distinctive to be differentiated easily from other materials such as may be present in blast debris. Spherical or at least generally spheroidal, cylindrical, polyhedral or other uniform geometric shapes are readily recognized and retrieved from common debris. For ease of handling and to avoid health hazards, the broadest dimension of each individual microparticle is preferably at least one micrometer (micron), but no more than 250 micrometers. Larger dimensions are likely to be uneconomical. A preferred size range for each of use and economy is 20 to 150 micrometers. To permit the microparticles to be uniformly dispersed throughout the substance to be tagged, the organic carrier is normally tack-free at ordinary room temperature (20°—25° C.).

Tack-free organic microspheres which have been recovered from the debris of a dynamite explosion in the practice of the present invention include polyethylene, specifically "Allied Chemical 617"; epoxy resin of relatively high molecular weight, specifically "Epon 1004"; carnauba wax; polystyrene; polyamide, specifically low-melting nylon; polyurethane, specifically a 2-part isocyanate-

glycol system; poly(trifluoromonochloro)-ethylene, specifically "Kel-F"; paraffin wax, specifically "Shellwax 700" ("Kel-F" is a registered Trade Mark). Other carriers which
5 have not been used but should be equally useful include polypropylene and other polyolefins such as poly-4-methyl pentene-1, polytetrafluoroethylene, polycarbonates, polyesters, polyisocyanurates, phenolic resins, acrylic
10 resins including ionomers such as ethylene-acrylic acid copolymers and candelilla wax (melting point 66°—71° C.) and other natural and synthetic waxes and resins which initially have a softening (melting) point below
15 200° C. so that they can readily be formed into microparticles of distinctive shape by known techniques such as melt-spinning. After the microparticles are formed, the carrier material may cure autogenously to an infusible,
20 insoluble state. For example, liquid phenolic or urethane compositions can be sprayed into a heated chamber wherein they rapidly congeal to provide thermoset microspheres, it being preferred for the practice of this invention that
25 the organic carrier be crosslinked, but not to the extent that it may become friable. The more highly crosslinked an organic material is, the less of any solvent it will imbibe. Microcrystalline character of the organic carrier is
30 also preferred over non-crystalline carrier materials since microcrystallinity generally confers insolubility in potential solvents such as nitroglycerine.

The organic carrier should not have a softening (melting) point below 60° C. (preferably
35 70° C.) in order to withstand detonation of the explosive with which it is mixed; although it should be noted that the temperature of detonation briefly far exceeds such softening
40 point without unduly distorting the distinctive shape of the microparticles. In view of the diverse classes of organic carriers which are useful in the present invention, the softening or melting point of each class should be de-
45 termined by a test method which is recognized as pertinent to that class (see Volumes 15, 18, 20, 26, 27, 29 and 30 of ASTM Test Methods, 1973 edition). The organic carrier is preferably of microcrystalline or crosslinked char-
50 acter so that it will not absorb nitroglycerine nor soften in common organic solvents which may be used in the process of isolating the microparticles.

Individual units of production of an ex-
55 plosive may be tagged for reprospective identification in accordance with the present invention by:

(1) providing microparticles of distinctive shape, which microparticles each comprise
60 a tack-free organic carrier which notes not have a softening point below 60° C. and contains one or more tagging elements each in an amount of at least 0.1 percent of the total weight;
65 (2) providing an inventory of batches of

microparticles, each batch being uniformly coded by incorporation in the microparticles of a selected combination of the tagging elements, which inventory in-
70 cludes up to

$$(L+1)^N - 1$$

uniquely coded batches of microparticles where L is the number of discrete concentration levels at which the individual elements are used and N is the number
75 of available tagging elements, and the microparticles of at least some of the batches contain at least three tagging elements:

(3) maintaining a record of particular ele-
80 ments and their levels employed in each batch of microparticles; and

(4) incorporating microparticles from any one batch with only one unit of production of the explosive, recovery and analysis of
85 a single microparticle being sufficient to identify the unit of production of the substance.

Each tagging element should be incorporated in an amount of at least 0.1 percent of the
90 total weight to provide an efficient analytical operation with an electron microprobe analyzer, the present instrument of choice. In the ultimate analysis, only the element itself is detected, and its existence is the microparticle
95 as a free element or as part of a compound is not differentiated. If desired, two elements may be provided by a single compound (e.g., $PbCrO_4$ or K_2AsO_4).

Because the beam of an electron microprobe
100 analyser may be very narrow compared to the thickness of a microparticle, it is preferred that the tagging elements be uniformly dispersed through each microparticle. If the tagging elements were not uniformly dispersed, it would
105 be difficult to obtain reliable quantitative analysis using the electron microprobe analyzer. Other analytical techniques which may be used do not depend upon uniform dispersion of the tagging elements for reliable quantitative
110 analysis, e.g., neutron activation analysis, atomic absorption spectroscopy, emission spectroscopy, energy-dispersive X-ray analysis, electron paramagnetic resonance spectrometry, and spark-source mass spectrometry. It is
115 sufficient for those techniques that the microparticles contain uniform amounts of the tagging elements. However, it is much preferred that the tagging elements be uniformly dispersed within each microparticle because the
120 electron microprobe analyzer it so easy to use, reliable and economical.

Because of practical limits with the present analytical instruments, it is believed that the concentration levels of one element should
125 vary from one batch of microparticles to the next by a factor of at least 1.5, a factor of 2 being preferred.

A small number of tagging elements, each used at a few concentration levels, provides a very large number of uniquely coded batches. An inventory of microparticles using combinations of ten selected elements at three discrete concentration levels such as 0.5%, 1% and 2% by weight would provide 1,048,575 different codes. A greater number of elements and/or a greater number of concentration levels would provide a correspondingly greater number of codes. By adding uniquely coded microparticles to each unit of production of a substance, recovery of a single microparticle indentifies the exact unit of production.

The tagging elements may be selected from any of the presently available chemical elements, but elements having high natural radioactivity would be generally excluded for health and ecology reasons. The following elements are preferred:

*Aluminium	*Nickel
*Antimony	*Niobium (Columbium)
*Arsenic	Osmium
*Barium	Palladium
*Bismuth	Platinum
*Cadmium	*Potassium
*Calcium	*Praseodymium
*Cerium	Rhenium
Cesium	Rhodium
*Chromium	Rubidium
*Cobalt	Ruthenium
*Copper	Samarium
Dysprosium	Scandium
Erbium	Selenium
Europium	*Silicon
Gadolinium	*Silver
*Gallium	*Sodium
*Germanium	*Strontium
Gold	*Tantalum
Hafnium	Tellurium
Holmium	Terbium
*Indium	Thallium
Iridium	*Thorium
*Iron	Thulium
*Lanthanum	*Tin
*Lead	*Titanium
*Lithium	*Tungsten (Wolfram)
Lutetium	*Uranium
*Magnesium	*Vanadium
*Manganese	Ytterbium
*Molybdenum	Yttrium
*Neodymium	*Zinc
	*Zirconium

The elements marked (*) are believed to have particular advantage because of economic considerations.

Isolation of the organic microparticles is enhanced if their specific gravity is in the range of 1.1 to 1.9. Within this range, lighter material can be floated away on water and then the microparticles can be recovered from the surface of a liquid having a specific gravity of at least 1.9. Since the specific gravity of many organic carriers approximates or is less than that of water, it may be desirable to mix a heavy material into the carrier to adjust its specific gravity to a desired level. Magnetite is especially useful in that it is inexpensive, and it enables magnetic separation to be used, if desired. If the magnetite is magnetized to permit magnetic separation of the microparticle from the debris, the microparticles might be difficult to separate from magnetic debris until demagnetized, e.g., in an A.C. field. On the other hand, an explosive before detonation would be free from any other magnetic material so that demagnetization would not be necessary.

Example 1.

Using a high-shear mixer at 150° C., a melt was prepared from 200 g polyethylene pellets, 73 g pigment-grade Cr_2O_3 and 427 g magnetite powder. The polyethylene ("Allied Chemical 617") had an average molecular weight of 1500 and a softening point (ASTM Method E 28) of 102° C. The melt was gravity fed to a spinning cup atomizer, the cup of which had a diameter of 9.4 cm at a sharp lip from which its inner wall tapered to a diameter of 4.4 cm at a depth of 5 cm. While the cup was heated to 170°—180° C. and rotated on a vertical shaft at 6000 rpm, the melt was fed at a rate of 40.7 g/min. Spherical microparticles, formed by cooling in ambient air as the atomized melt left the rim of the spinning cup, were 25 to 170 micrometers in diameter and 1.4 to 1.5 in specific gravity. The yield of microspheres was 94%. The primary tagging element, chromium, was uniformly present in each microsphere, providing 2.0 percent of the total weight. The iron of the magnetite could also be employed as a tagging element, but it is preferred that each tagging element provide 0.5, 1.0, 2.0 or 4.0 percent by weight of the particle.

A one gram sample of the 2% Cr-tagged polyethylene microspheres was hand-mixed with one-half pound (225 g) sticks of dynamite, which were then repacked. A #6 blasting cap was inserted and the dynamite was detonated on open ground.

Debris collected from the crater and its immediate surroundings was air-dried in an aluminium foil baking pan and screened first through a 20-mesh sieve (nominal openings of 840 micrometers) and then through a 60-mesh sieve (nominal openings of 250 micrometers). Approximately 6 g of these fines were placed in a beaker, wetted with acetone and mixed into a 250-ml glass cylinder with jets of de-aerated water from a plastic wash bottle. [Tap water releases tiny air bubbles which can carry microparticles to the surface]. The nearly full cylinder was stirred thoroughly and allowed to stand at least two minutes. The turbid supernatant was decanted to waste, additional deaerated water added, and the process repeated until the supernatant water was essentially clear.

After carefully transferring the sludge to a 150-ml beaker using jets of deaerated water, the solids were again allowed to settle. The clear supernatant was decanted as completely as possible to waste, and the sludge was dispersed thoroughly in about 75 ml of saturated zinc chloride solution in water (sp. gr. 1.9). The turbid solution was decanted equally into two 15-ml centrifuge tubes, spun one minute in a centrifuge at 700—900 rpm, and the thin layer of dark particulate matter at the top of the fluid was removed to a 5-cm Petri dish with a medicine dropper. This concentrate was diluted and washed with deaerated, distilled water several times by careful decantation to free the solid concentrate of zinc chloride. A few drops of concentrated hydrochloric acid were added to the first rinse to prevent hydrolysis of the $ZnCl_2$. The now-solid concentrate was rinsed twice with acetone to reduce the water content and allowed to dry in air.

When dry, inspection under a stereomicroscope at 60 × magnification revealed numerous black microspheres, indicating that far less than one gram of the microspheres would have been more than adequate for retrospective identification. Removal of five microspheres with a very sharp dissecting needle to an adhesive-coated mounting disk permitted analysis by the electron microprobe analyzer to reveal the presence of 2% chromium as well as the iron in the magnetite.

A preliminary screening test indicates that these microspheres may reduce the sensitivity of dynamite to impact. Used in the test was 85% dynamite into which was thoroughly dispersed various amounts of the polyethylene microspheres. In this test, a metal cup with a cylindrical opening 5 mm in diameter and 5 mm in depth was filled with 20 mg of the dynamite mixture to be tested. A 2-kg plummet was dropped 100 cm onto a steel pin positioned to be driven into the cup, with the following results:

Parts by weight microspheres per 100 parts dynamite	Number of detonations in 10 samples
0	6
1	3
25	0

When one part by weight of glass microspheres was added per 100 parts of dynamite, there were seven detonations out of ten samples.

Examples 2—13.

Using the same polyethylene, microspheres were prepared in the same maner as in Example 1, except as indicated below. In each case the microspheres were within the range of 25—170 micrometers diameter and had a specific gravity in the range of 1.4 to 1.5.

Example	Weight % of Polyethylene	Weight % of Magnetite	Additives	Weight % of Additives	Weight % of Tagging Elements
2	80	18	CoO	2.0	1.42 Co
3	80	18	NiO	2.0	1.57 Ni
4	80	18	CdO	2.0	1.75 Cd
5	70	29.27	Cr_2O_3	0.73	0.5 Cr
6	70	28.55	Cr_2O_3	1.45	1.0 Cr
7	70	24.2	Cr_2O_3	5.8	4.0 Cr
8	70	27.23	{ $BaCrO_4$ / Cr_2O_3	{ 1.85 / 0.92 }	{ 1.0 Ba / 1.0 Cr
9	70	28.7	CdS	1.3	1.0 Cd
10	70	28.33	TiO_2	1 67	1.0 Ti
11	70	28.56	$BaCO_3$	1.44	1.0 Ba
12	70	28.75	CuO	1.25	1.0 Cu
13	70	28.72	$PbSO_4$	1.28	0.87 Pb

Example 14.

Microspheres were made as in Example 1 except substituting carnauba wax for the polyethylene. Carnauba wax is a tack-free solid having a melting range of 80°—86° C. and a specific gravity of 0.990—0.999 at 15° C. The wax being more fluid than the polyethylene, the spinning cup atomizer was operated at 5000 rpm and 135° C. at a feed rate of 200 g/min. The resulting microspheres had a diameter of 17—170 micrometers and contained 70% by weight of carnauba wax, 27.1% by weight of magnetite and 2.9% by weight of Cr_2O_3 to provide 2% Cr as the primary tagging element. The specific gravity was 1.4 to 1.5.

Example 15.

Microspheres 20—200 micrometers in diameter were prepared as described in Example 14 except that the carnauba wax was replaced by a paraffin wax, specifically, "Shellwax 700", a fully refined paraffin wax having a melting point of 84° C. (ASTM D—27). Since the waxes of both Examples 14 and 15 are of a microcrystalline character, they do not absorb nitroglycerine. The microparticles of each example were recovered from dynamite after detonation.

Example 16.

Microspheres 60—100 micrometers in diameter were made from 40 parts by weight of epoxy resin and 60 parts of magnetite by the method of Example 1 except that the cup speed was 6100 rpm at 115° C., the feed temperature was 150° C. and the feed rate was 140 g/min. The specific epoxy resin was a condensation product of 2,2-bis(4-hydroxyphenyl) propane and epichlorohydrin having an epoxide equivalent weight of about 875—1000 and a Durrans' softening point of 95°—105° C. ("Epon 1004"). Because the epoxy resin is of a polar character; i.e., different portions have different charges, and therefore has a significant dipole moment, these microspheres are softened by polar substances such as nitroglycerine, methanol and acetone, thus restricting their use with dynamite and making extraction from debris more difficult. Nevertheless, these microspheres were successfully recovered from dynamite after detonation, apparently because of the short time period between admixture with the dynamite and the subsequent detonation.

WHAT WE CLAIM IS:—
1. An explosive composition, comprising
(A) explosive material; and
(B) microparticles of a tack-free organic carrier which does not have a softening point below 60° C., which microparticles have a distinctive shape, contain one or more tagging elements each in an amount of at least 0.1 percent of the total weight, and which are capable of surviving detonation of the explosive material and so permit retrospective identification of the explosive although it has been detonated.

2. An explosive composition according to Claim 1 wherein the microparticles are of generally spheroidal shape.

3. An explosive composition according to Claim 1 or Claim 2 wherein the broadest dimension of each individual microparticle is in the range of 1 to 250 micrometers.

4. An explosive composition according to Claim 3 wherein substantially all of the microparticles have a broadest dimension of between 20 and 150 micrometers.

5. An explosive composition according to any preceding claim wherein the specific gravity of the particles is 1.1 to 1.9.

6. An explosive composition according to any preceding claim wherein the tagging elements are uniformly dispersed throughout each microparticle to permit easy and reliable qualitative and quantitative analysis of the tagging elements by electron microprobe analysis of a microparticle.

7. An explosive composition according to any preceding claim wherein the explosive material is dynamite and the organic carrier is so selected that it is not softened by substances having a significant dipole moment.

8. An explosive composition substantially as described in any one of the examples herein.

9. A method of tagging individual units of production of an explosive comprising the steps of:
(1) providing microparticles of distinctive shape, which microparticles each comprise a tack-free organic carrier which does not have a softening point below 60° C. and contains one or more tagging elements each in an amount of at least 0.1 percent of the total weight;
(2) providing an inventory of batches of microparticles, each batch being uniformly coded by incorporation in the microparticles of a selected combination of the tagging elements, which inventory includes up to

$$(L+1)^N - 1$$

uniquely coded batches of microparticles where L is the number of discrete concentration levels at which the individual elements are used and N is the number of available tagging elements, and the microparticles of at least some of the batches contain at least three tagging elements:
(3) maintaining a record of particular elements and their levels employed in each batch of microparticles; and
(4) incorporating microparticles from any one batch with only one unit of production

of the explosive, recovery and analysis of a single microparticle being sufficient to identify the unit of production of the substance.

10. A method of tagging individual units of production of an explosive according to Claim 9 wherein each microparticle is spheroidal.

11. A method according to Claim 9 or Claim 10 wherein the broadest dimension of each individual microparticle is in the range of 1 to 250 micrometers.

12. A method according to Claim 11 wherein substantially all of the microparticles have a broadest dimension of between 20 and 150 micrometers.

13. A method according to any of Claims 9 to 12 wherein N is at least 10 and L is at least 3.

14. A method according to any of Claims 9 to 13 wherein the organic carrier is a polymer or a wax.

15. A method according to any of Claims 9 to 14 wherein the organic carrier is microcrystalline and/or crosslinked.

16. A method according to any of Claims 9 to 15 wherein the organic carrier has a softening point in the range of 70 to 200° C.

17. A method according to any of Claims 9 to 16 wherein the organic carrier is selected from the group consisting of polyolefin, epoxy resin, polystyrene, polyamide, polyurethane, poly(trifluoromonochloro)ethylene, polytetrafluoroethylene, polycarbonate, polyester, polyisocyanurate, phenolic resin, acrylic resin, candelilla wax, carnauba wax and paraffin wax.

18. A method according to any of Claims 9 to 17 wherein the or each tagging element is selected from Ba, Cd Co, Cr, Cu, Fe, Ni, Pb and Ti.

19. A method substantially as herein described of tagging individual units of production of an explosive.

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